Ruthenium Tripyrazolylborate Complexes. 9.[1] Formation and Characterization of Amidocarbene Complexes

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The complexes of the RuTpCl fragment with the mixed bidentate ligands 2-acetamidopyridine (Haapy), 2-acetamido-4-methylpyridine (4-Me-Haapy), and 1-ethyl-2-acetamido-4-methylpyridine (N-Et-4-Me-Haapy) are synthesized and their reactions with acetylenes are described. RuTp(Haapy)Cl (**2a**) reacts in an unexpected manner with HC≡CR (R = Ph, *n*-Bu) to give cyclic amido carbene complexes RuTp(=CCH$_2$R-aapy)Cl (**3**, **4**). In the case of R = C(Me)(Ph)OH and C_6H_{11} the vinylcarbene complexes RuTp(=CCH=C(Me)Ph-aapy)Cl (**5**) and RuTp(=CCH=C_6H_{10}-aapy)Cl (**6**) are obtained, and with R = COOEt and COOMe the olefin complexes RuTp(aapy-CH=CHCOOEt)Cl (**7**) and RuTp(aapy-CH=CHCOOMe)Cl (**8**) are formed. Solvates of complexes **2b** and **3** are characterized by X-ray crystallography.

Introduction

Transition-metal vinylidene complexes have been the subject of considerable recent investigation. Interest in these compounds stems from their potential as reactive intermediates in organic and organometallic synthesis as well as their application in catalytic processes.[2] A key characteristic of vinylidene complexes appears to be the electrophilicity of the α-carbon, which adds, often easily, amines,[2d,3] alcohols,[2c,3,4] phosphines,[5] and even fluoride.[2c]

In the course of our studies of ruthenium hydridotris(pyrazolyl)borate complexes we recently reported on the chemistry of the complexes RuTp(PPh_3)(vinylidene)Cl[6] and RuTp(PCy_3)(vinylidene)Cl[7] and their application to the catalytic dimerization of terminal acetylenes.[8] In these complexes, the phosphine ligand is bonded very strongly to the ruthenium center, making this coordination site unavailable for an incoming substrate. In contrast, the complex RuTp($py)_2$Cl was found to lead to the polymerization of terminal acetylenes,[8b] likely via the intermediacy of [RuTp(py)(vinylidene)Cl]. To elucidate the differences in behavior between P and N donor ligands further, we attached some hemilabile N−O ligands to the RuTpCl fragment and reacted these complexes with acetylenes. However, instead of obtaining neutral vinylidene complexes bearing a stable N donor coligand, we observed rather unexpected reactions, and these are reported here.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified argon by using Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[9] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. RuTp(COD)Cl (**1**), 2-acetamidopyridine (Haapy), 2-acetamido-4-methylpyridine (4-Me-Haapy),

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and 1-ethyl-2-acetamido-4-methylpyridine (N-Et-4-Me-Haapy) were prepared according to the literature.[10,11] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalyses were done by Microanalytical Laboratories, University of Vienna.

Synthesis. RuTp(Haapy)Cl (2a). A solution of **1** (517 mg, 1.129 mmol) and 2-acetamido-pyridine (160 mg, 1.175 mmol) in DMF (3 mL) was heated under reflux for 2 h. The solvent was then removed under vacuum, and the resulting residue was washed several times with diethyl ether and dried under vacuum. Yield: 534 mg (97%). Anal. Calcd for $C_{16}H_{18}BClN_8ORu$: C, 39.57; H, 3.74; N, 23.07. Found: C, 39.64; H, 3.79; N, 23.00. ^{1}H NMR (δ, $CDCl_3$/DMSO-d_6 (20/1), 20 °C): 11.18 (s, 1H, NH), 7.44−7.32 (m, 5H, Tp, py^6), 7.11−7.07 (m, 2H, py^3, Tp), 6.71 (m, 1H, py^4), 6.40 (s, 1H, Tp), 6.20 (m, 1H, py^5), 5.85 (m, 1H, Tp), 5.78 (m, 1H, Tp), 5.73 (m, 1H, Tp), 1.90 (s, 3H, $COCH_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$/DMSO-d_6 (20/1), 20 °C): 172.0 (N*C*OCH$_3$), 154.6 (py^1), 151.2 (py^5), 144.7 (Tp), 142.7 (Tp), 141.8 (Tp), 135.8 (Tp), 135.5 (Tp), 134.8 (Tp), 134.6 (py^3), 118.72 (py^4), 113.9 (py^2), 105.8 (2Tp), 105.4 (Tp), 24.2 (NCO*C*H$_3$). IR (KBr, cm^{-1}): 1656 (s, $\nu_{C=O}$), 2471 (w, ν_{B-H}).

RuTp(4-Me-Haapy)Cl (2b). This compound was prepared analogously to **2a** with **1** and 2-acetamido-4-methylpyridine as the starting materials. Yield: 90%. Anal. Calcd for $C_{17}H_{20}BClN_8ORu$: C, 40.86; H, 4.03; N, 22.42. Found: C, 40.99; H, 4.23; N, 22.36. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 12.36 (bs, 1H, NH), 7.96−7.70 (m, 6H, Tp, py^6), 7.32 (bs, 1H, py^3), 6.79 (bs, 1H, Tp), 6.43 (d, J = 5.6 Hz, 1H, py^5), 6.37 (m, 1H, Tp), 6.30 (m, 1H, Tp), 6.15 (m, 1H, Tp), 2.42 (s, 3H, py-*Me*), 2.15 (s, 3H, $COCH_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$ (20/1), DMSO-d_6, 20 °C): 172.1 (N*C*OCH$_3$), 154.7 (py^2), 150.9 (py^4), 150.8 (py^6), 144.8 (Tp), 142.7 (Tp), 141.9 (Tp), 135.6 (Tp), 135.5 (Tp), 134.8 (Tp), 120.7 (py^5), 114.6 (py^3), 105.8 (Tp), 105.7 (Tp), 105.4 (Tp), 24.2 (NCO*C*H$_3$), 22.4 (Me).

RuTp(N-Et-4-Me-Haapy)Cl (2c). This compound was prepared analogously to **2a** with **1** and 1-ethyl-2-acetamido-4-methylpyridine as the starting materials. Yield: 89%. Anal. Calcd For $C_{19}H_{24}BClN_8ORu$: C, 43.24; H, 4.58; N, 21.23. Found: C, 43.30; H, 4.67; N, 21.02. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.96 (1H, Tp), 7.79−7.72 (m, 3H, Tp, py^6), 7.59−7.52 (m, 2H, Tp, py^5), 6.98 (bs, 1H, py^3), 6.43 (d, J = 5.6 Hz, 1H, py^5), 6.52 (m, 1H, Tp), 6.30 (m, 1H, Tp), 6.18 (m, 1H, Tp), 6.07 (m, 1H, Tp), 4.27−4.06 (m, 2H, C*H*$_2$CH$_3$), 2.49 (s, 3H, py-*Me*), 2.27 (s, 3H, $COCH_3$), 1.64 (q, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 183.4 (N*C*OCH$_3$), 156.3 (py^6), 154.7 (py^2), 146.7 (py^4), 145.9 (Tp), 144.1 (Tp), 142.1 (Tp), 136.4 (Tp), 136.3 (Tp), 135.8 (Tp), 122.7 (py^5), 116.8 (py^3), 107.0 (Tp), 106.6 (Tp), 106.5 (Tp), 48.7 (CH_2CH_3), 27.0 (NCO*C*H$_3$), 21.6 (py-Me), 15.0 CH_2CH_3).

RuTp(=CCH$_2$Ph-aapy)Cl (3). To a suspension of **2a** (100 mg, 0.206 mmol) in toluene (5 mL) was added HC≡CPh (200 μL), and the mixture was heated at reflux for 20 h. The solvent was then removed under vacuum, and the crude product was deposited on a dry 5-cm column of silica gel. The column was first eluted with CH_2Cl_2 (colorless solution) and then with 1/1 (v/v) CH_3CN/CH_2Cl_2 (brown solution). The latter solvent was removed by rotary evaporation, resulting in a brown solid, which was washed with diethyl ether and dried under vacuum. Yield: 103 mg (85%). Anal. Calcd for $C_{24}H_{24}BClN_8ORu$: C, 49.04; H, 4.12; N, 19.06. Found: C, 49.12; H, 4.23; N, 18.96. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.39 (d, J = 5.9 Hz, 1H, py), 8.27 (d, J = 2.1 Hz, 1H, Tp), 7.97 (d, J = 2.1 Hz, 1H, Tp), 7.86 (d, J = 2.1 Hz, 1H, Tp), 7.81 (d, J = 2.5 Hz, 1H, Tp), 7.71 (dd, J = 8.4 Hz, J = 7.1 Hz, 1H, py), 7.55 (d, J = 2.5 Hz, 1H, Tp), 7.45 (d, J = 8.4 Hz, 1H, py), 7.09 (dd, J = 5.8 Hz, J = 7.1 Hz,1H, py), 7.05 (m, 3H, Ph), 6.92−6.88 (m, 2H, Ph), 6.45 (vt, J = 2.1 Hz, Tp), 6.28 (vt, J = 2.4 Hz, 1H, Tp), 5.63 (vt, J = 2.1 Hz, 1H, Tp), 5.31 (d, J = 2.1 Hz, 1H, Tp), 5.12 (d, J = 13.9 Hz, 1H, C*H*$_2$), 4.76 (d, J = 13.9 Hz, 1H, C*H*$_2$), 2.51 (s, 3H, COC*H*$_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 288.0 (Ru=*C*), 177.7 (N*C*OCH$_3$), 158.0 (py^1), 152.1 (py^5), 145.1 (py^3), 142.8 (Tp), 141.5 (Tp), 137.5 (Tp), 137.5 (Tp), 135.9 (Tp), 135.5 (Tp), 135.1 (Ph^1), 130.3 (Ph^{3,5}), 129.0 (Ph^{2,6}), 126.9 (Ph^4), 120.2 (py^4), 111.4 (py^2), 106.9 (Tp), 106.7 (Tp), 106.1 (Tp), 52.4 (*C*H$_2$Ph), 29.4 (NCO*C*H$_3$). IR (KBr, cm^{-1}): 1748 (s, $\nu_{C=O}$), 2469 (w, ν_{B-H}).

RuTp(=CCH$_2$Bu^n-aapy)Cl (4). This compound was prepared analogously to **3** using **2a** and HC≡CBu^n as the starting materials. The reaction was performed in THF as the solvent. Yield: 100 mg (65%). Anal. Calcd for $C_{22}H_{28}BClN_8ORu$: C, 46.53; H, 4.97; N, 19.73. Found: C, 46.60; H, 5.09; N, 19.45. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.45 (d, J = 5.7 Hz, 1H, py), 8.28 (d, J = 1.8 Hz, 1H, Tp), 7.95 (d, J = 1.8 Hz, 1H, Tp), 7.92 (d, J = 2.1 Hz, 1H, Tp), 7.82 (d, J = 2.5 Hz, 1H, Tp), 7.56 (dd, J = 8.6 Hz, J = 7.5 Hz, 1H, py), 7.73 (d, J = 2.5 Hz, 1H, Tp), 7.62 (d, J = 8.6 Hz, 1H, py), 7.12 (dd, J = 5.7 Hz, J = 7.5 Hz,1H, py), 6.49 (vt, J = 2.0 Hz, Tp), 6.33 (dd, J = 2.5, J = 1.8 Hz, 1H, Tp), 5.91 (vt, J = 2.5 Hz, 1H, Tp), 5.76 (d, J = 2.1 Hz, 1H, Tp), 4.00 (m, 1H, C*H*$_2$), 3.18 (m, 1H, Ru=CC*H*$_2$), 2.88 (s, 3H, COC*H*$_3$), 1.03 (m, 6H, C*H*$_2$), 0.69 (t, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 293.5 (Ru=*C*), 177.4 (N*C*OCH$_3$), 157.6 (py^1), 152.1 (py^5), 145.0 (py^3), 142.8 (Tp), 142.2 (Tp), 137.4 (Tp), 136.4 (Tp), 135.7 (Tp), 135.6 (Tp), 120.4 (py^4), 112.0 (py^2), 106.8 (Tp), 106.6 (Tp), 105.9 (Tp), 49.7 (Ru=C*C*H$_2$), 32.5, 30.1 (NCO*C*H$_3$), 26.3, 22.6, 14.2 (*C*H$_3$).

RuTp(=CCH=C(Me)Ph-aapy)Cl (5). This compound was prepared analogously to **3** with **2a** and HC≡CCMe(Ph)OH (1-phenyl-3-butyn-1-ol) as the starting materials. Yield: 92 mg (73%). Anal. Calcd for $C_{26}H_{26}BClN_8ORu$: C, 50.87; H, 4.27; N, 18.25. Found: C, 51.02; H, 4.36; N, 18.03. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.33 (d, J = 5.6 Hz, 1H, py), 8.29 (d, J = 2.2 Hz, 1H, Tp), 8.25 (d, J = 8.2 Hz, 1H, py), 7.92 (d, J = 2.2 Hz, 1H, Tp), 7.90 (m, 1H, py), 7.79 (d, J = 1.9 Hz, 1H, Tp), 7.76 (d, J = 2.2 Hz, 1H, Tp), 7.71 (d, J = 2.2 Hz, 1H, Tp), 7.36−7.18 (m, 6H, Ph, C*H*=CMe*Ph*), 7.12 (dd, J = 7.2 Hz, J = 5.8 Hz, 1H, py), 6.48 (vt, J = 2.1 Hz, Tp), 6.22 (vt, J = 2.1 Hz, 1H, Tp), 5.91 (vt, J = 2.1 Hz, 1H, Tp), 5.82 (d, J = 2.2 Hz, 1H, Tp), 2.74 (s, 3H, COC*H*$_3$), 1.69 (s, 3H, Me). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 293.9 (Ru=*C*), 174.2 (N*C*OCH$_3$), 157.1 (py^1), 151.5 (py^5), 145.6 (py^3), 142.8 (Tp), 142.7 (C=*C*MePh), 141.4 (Tp), 139.1 (Tp), 138.3 (Tp), 137.8 (Tp), 136.5 (Tp), 135.4 (*C*=CMePh), 129.9 (Ph^1), 129.2 (Ph^{3,5}), 128.4 (Ph^4), 126.2 (Ph^{2,6}), 121.0 (py^4), 113.9 (py^2), 106.8 (Tp), 106.4 (Tp), 106.3 (Tp), 30.0 (NCO*C*H$_3$), 18.4 (Me).

RuTp(=CCH=C$_6$H$_{10}$-aapy)Cl (6). This compound was prepared analogously to **3** with **2a** and HC≡CC$_6$H$_9$ (1-cyclohexenylethyne) as the starting materials. Yield: 123 mg (92%). Anal. Calcd for $C_{24}H_{28}BClN_8ORu$: C, 48.70; H, 4.77; N, 18.93. Found: C, 48.75; H, 4.76; N, 18.78. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.24−8.20 (m, 3H, py, Tp), 7.89 (d, J = 2.2 Hz, 1H, Tp), 7.80−7.64 (m, 4H, Tp, py), 7.07 (dd, J = 6.6 Hz, J = 7.1 Hz, 1H, py), 6.83 (s, 1H, Ru=CC*H*=), 6.45 (vt, J = 2.2 Hz, Tp), 6.23 (vt, J = 2.4 Hz, 1H, Tp), 5.88 (vt, J = 2.2 Hz, 1H, Tp), 5.67 (d, J = 2.2 Hz, 1H, Tp), 2.71 (s, 3H, COC*H*$_3$), 1.98−1.10 (m, 10H). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 286.6 (Ru=*C*), 174.2 (N*C*OCH$_3$), 156.8 (py^1), 151.4 (py^5), 145.5 (py^3), 142.9 (Tp), 141.6 (Tp), 138.2 (Tp), 137.8 (Tp), 136.6 (=C), 136.5 (Tp), 136.46 (Tp), 135.8, 135.4 (Tp, Ru=CCH), 120.7 (py^4), 113.9 (py^2), 106.8 (Tp), 106.3 (Tp), 106.1 (Tp), 38.1 (CH_2), 31.7 (CH_2), 30.5 (NCO*C*H$_3$), 28.0 (CH_2), 27.5 (CH_2), 26.6 (CH_2).

RuTp(aapy-CH=CHCOOEt)Cl (7). A suspension of **1** (100 mg, 0.206 mmol) in THF (5 mL) was treated with 100 μL of HC≡CCOOEt and heated at reflux for 24 h. The solvent was then removed under vacuum, and the crude product was dissolved in CH_2Cl_2 (1 mL). On addition of diethyl ether a precipitate was formed, which was collected on a glass frit,

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washed with diethyl ether, and dried under vacuum. Yield: 107 mg (89%). Anal. Calcd for $C_{21}H_{24}BClN_8O_3Ru$: C, 43.20; H, 4.14; N, 19.19. Found: C, 43.37; H, 4.20; N, 19.18. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.06 (d, J = 8.1 Hz, 1H, py^6), 7.88−7.86 (m, 2H, Tp), 7.80 (d, J = 3.0 Hz, 1H, Tp), 7.79 (d, J = 8.8 Hz, 1H, CH=C*H*COOEt), 7.63 (m, 1H, py), 7.61 (d, J = 2.6 Hz, 1H, Tp), 7.32 (d, J = 2.5 Hz, 1H, Tp), 7.30 (d, J = 7.4 Hz, 1H, py), 6.82 (dd, J = 8.1 Hz, J = 7.3 Hz, 1H, py), 6.74 (d, J = 1.8 Hz, 1H, Tp), 6.36 (vt, J = 2.2 Hz, Tp), 6.28 (vt, J = 2.4 Hz, 1H, Tp), 6.12 (vt, J = 2.2 Hz, 1H, Tp), 3.65 (d, J = 8.8 Hz, 1H, C*H*=CHCOOEt), 3.50−3.27 (m, 2H, diasterotopic CH_2), 2.82 (s, 3H, COC*H*$_3$), 0.51 (t, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 171.8, 171.75 (*C*OOEt, N*C*OCH$_3$), 157.5 (py^1), 151.9 (py^5), 146.6 (py^3), 144.1 (Tp), 143.7 (Tp), 138.0 (Tp), 137.3 (Tp), 135.9 (Tp), 135.6 (Tp), 120.9, 120.0 (py^4, py^2), 107.2 (Tp), 107.1 (Tp), 106.5 (Tp), 99.9 (*C*H=CHCOOEt), 60.3 (CH=*C*HCOOEt), 60.0 (COO*C*H$_2$CH$_3$), 25.5 (NCO*C*H$_3$), 13.9 (COOCH$_2$*C*H$_3$).

RuTp(aapy-CH=CHCOOMe)Cl (8). To a suspension of **1** (180 mg, 0.371 mmol) in THF (5 mL) was added 150 μL of HC≡COOMe, and the mixture was heated at reflux for 24 h. After removal of the solvent, the crude product was dissolved in CH_2Cl_2. Addition of a 1/1 (v/v) mixture of diethyl ether/*n*-hexane afforded analytically pure **8**. Yield: 192 mg (91%). Anal. Calcd for $C_{20}H_{22}BClN_8O_3Ru$: C, 42.16; H, 3.89; N, 19.67. Found: C, 42.22; H, 4.00; N, 19.48. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.09 (d, J = 8.3 Hz, 1H, py^6), 7.88−7.86 (m, 2H, Tp), 7.79 (m, 1H, Tp), 7.81 (d, J = 9.3 Hz, 1H, CH=C*H*COOMe), 7.68−7.61 (m, 2H, py, Tp), 7.34−7.31 (m, 2H, Tp, py), 6.82 (ddd, J = 6.1 Hz, J = 7.3 Hz, J = 0.9 Hz, 1H, py), 6.74 (d, J = 2.3 Hz, 1H, Tp), 6.36 (vt, J = 2.3 Hz, Tp), 6.30 (vt, J = 2.3 Hz, 1H, Tp), 6.13 (vt, J = 2.8 Hz, 1H, Tp), 3.63 (d, J = 9.3 Hz, 1H, C*H*=CHCOOMe), 2.97 (s, 3H, COOC*H*$_3$), 2.83 (s, 3H, COC*H*$_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 172.5 (*C*OOMe), 171.8 (N*C*OCH$_3$), 157.6 (py^1), 152.0 (py^5), 146.6 (py^3), 144.0 (Tp), 143.7 (Tp), 138.1 (Tp), 137.5 (Tp), 136.1 (Tp), 135.7 (Tp), 120.9, 120.1 (py^4, py^2), 107.3 (Tp), 107.1 (Tp), 106.3 (Tp), 99.8 (*C*H=CHCOOMe), 59.9 (CH=*C*HCOOMe), 51.8 (COO*C*H$_3$), 25.6 (NCO*C*H$_3$).

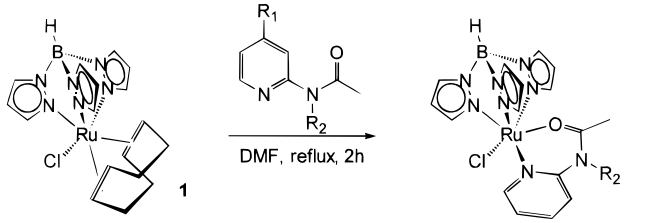
X-ray Structure Determination for 2b·CH_2Cl_2 and 3·$^1/_2O(C_2H_5)_2$. Well-crystallized solvates of **2b** and **3** were obtained by diffusion of diethyl ether into CH_2Cl_2 solutions. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.690 Å, a nominal crystal-to-detector distance of 3.85 cm, 0.3° ω-scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structures of **2b**·CH_2Cl_2 and **3**·$^1/_2O(C_2H_5)_2$ were solved by direct methods and by Patterson methods, respectively, using the program SHELXS86.[12] Structure refinement on F^2 was carried out with the program SHELXL93.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

Table 1. Crystallographic Data for RuTp(Me-Haapy)Cl·CH_2Cl_2 (2b·CH_2Cl_2) and RuTp(=CCH_2Ph-aapy)Cl·$^1/_2O(C_2H_5)_2$ (3·$^1/_2O(C_2H_5)_2$)

formula	$C_{17}H_{20}BClN_8O_2Ru$[a]	$C_{52}H_{58}B_2Cl_2N_{16}O_3Ru_2$
fw	515.74[a]	1249.80
cryst size, mm	0.32 × 0.20 × 0.06	0.48 × 0.24 × 0.08
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	11.957(5)	12.755(3)
b, Å	12.525(5)	13.655(3)
c, Å	17.164(7)	16.752(4)
α, deg		83.47(1)
β, deg	106.13(1)	75.91(1)
γ, deg		89.88(1)
V, Å^3	2469(2)	2810.6(11)
Z	4	2
ρ_{calc}, g cm^{-3}	1.387[a]	1.477
T, K	300(2)	298(2)
μ(Mo Kα), mm^{-1}	0.70[a]	0.690
abs cor	empirical	empirical
F(000)	1040[a]	1276
transmissn factors, min/max	0.704−0.894	0.682−0.928
θ_{max}, deg	27	30
index ranges	$-15 \le h \le 15$ $-16 \le k \le 15$ $-21 \le l \le 22$	$-8 \le h \le 17$ $-18 \le k \le 19$ $-23 \le l \le 23$
no. of rflns measd	23 497	22 562
no. of unique rflns	5369	15 495
no. of rflns $F > 4\sigma(F)$	3784	11 910
no. of params	304	695
R1 ($F > 4\sigma(F)$)[b]	0.0330	0.0328
R1 (all data)[b]	0.0645	0.0522
wR2 (all data)[b]	0.0799	0.0802
diff Fourier peaks min/max, e Å^{-3}	−0.315/0.383	−0.685/0.506

[a] CH_2Cl_2 solvent molecule of **2b**·CH_2Cl_2 was omitted from the marked data because of distinct disorder and partial occupancy (~50%). [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

Scheme 1



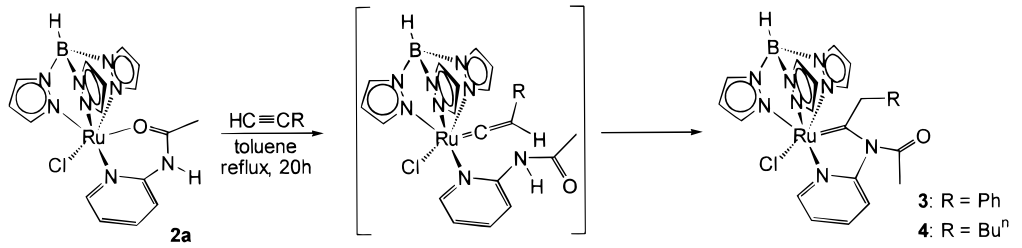
Results and Discussion

Synthesis of (2-Acetamidopyridine)ruthenium Tp Complexes. Treatment of RuTp(COD)Cl (**1**) with 1 equiv of 2-acetamidopyridine (Haapy) in boiling DMF for 2 h affords RuTp(Haapy)Cl (**2a**) in 97% isolated yield (Scheme 1) as a thermally robust air-stable red solid. Characterization of **2a** was by a combination of elemental analysis and IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In the IR spectrum of complex **2a** the ν(CO) band is observed at 1656 cm^{-1} (to be compared to 1668 cm^{-1} in free 2-acetamidopyridine), suggesting N,O rather than N,N coordination of the Haapy ligand. The ν(B−H) vibration is found at 2471 cm^{-1}, which is characteristic of Tp terdentate N,N′,N″-bonded to a metal center. Characteristic solution ^{1}H NMR spectroscopic data for **2a** include a singlet at 11.18 ppm assigned to the proton of the secondary amide of the Haapy moiety. In the ^{13}C{^{1}H} NMR spectrum, the ketonic carbonyl carbon is revealed by a resonance at 172.0 ppm. All other resonances are unremarkable. Attempts to grow crystals of **2a** suitable for X-ray crystallography were unsuccessful unless the methyl derivative RuTp(4-Me-Haapy)Cl (**2b**), prepared analogously, was taken. In this case suitable crystals could be grown from a CH_2Cl_2 solution layered with diethyl ether. The molecular structure of **2b**·CH_2Cl_2 depicted in Figure 1 confirms

(12) Sheldrick, G. M. SHELXS86: Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1986.

(13) Sheldrick, G. M. SHELXL93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

Scheme 2



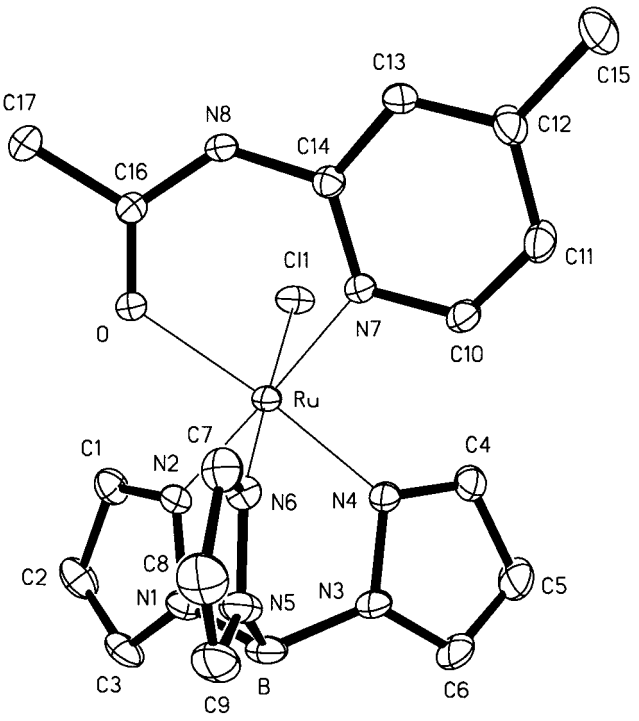


Figure 1. Structural view of RuTp(Me-Haapy)Cl·CH_2Cl_2 (**2b**·CH_2Cl_2). Selected bond lengths (Å) and angles (deg): Ru−N(2), 2.051(2); Ru−N(4), 2.040(2); Ru−N(6), 2.022(2); Ru−N(7), 2.072(2); Ru−O 2.080(2); Ru−Cl(1), 2.441(1); O−C(16), 1.222(3); C(16)−N(8), 1.349(3); N(8)−C(14), 1.412(3); C(14)−N(8)−C(16), 130.2(2); N(8)−C(16)−O, 124.2(3); N(6)−Ru−N(4), 88.1(1); N(6)−Ru−N(2), 89.1(1); N(4)−Ru−N(2), 84.5(1); N(6)−Ru−N(7), 89.8(1); N(7)−Ru−O 88.3(1); O−Ru−Cl(1), 89.8(1).

that Haapy is N,O-bonded. The crystal structure contains pairs of inversion-related complexes that are linked via two N−H···Cl hydrogen bonds (N(8)−Cl(1) 3.172 Å) to form a dimeric species. The coordination geometry of **2b** is approximately octahedral with all angles at ruthenium being between 88 and 97° and 174 and 178°. The three Ru−N(Tp) bond lengths show only small deviations from the average distance of 2.038(2) Å, which is within the range for other ruthenium Tp complexes.[6,10,14] The Ru−O distance and the Ru−O−C(16) angle are 2.080(2) Å and 125.1(2)°, respectively. The Ru−Cl(1) bond of 2.441(1) Å is slightly longer than that in other Ru(II) Tp complexes, e.g., 2.409(3) Å in [RuTp(PPh_3)$_2$(Cl)],[15] 2.401(1) Å in [RuTp(PPh_3)(Cl)(=C=CHPh)],[8a] and 2.418(2) Å in [RuTp(PPh_3)(Cl)(CO)].[6] For the 4-Me-Haapy moiety, the pattern of short N(8)−C(16) (1.349(3) Å) and long C(16)−O (1.222(3) Å) distances points to the involvement of the dipolar imine structure (e.g. in **3** the corresponding bond distances N(8)−C(15) and C(15)−O(1) are 1.465(3) and 1.176(3) Å, respectively).

Reaction with Acetylenes. The reaction of **2a** with HC≡CR (R = Ph, *n*-Bu) in THF at elevated temperatures did not yield the expected neutral vinylidene complexes RuTp(Haapy)(=C=CHR)Cl but the amidocarbene complexes RuTp(=CCH_2R-aapy)Cl (**3**, **4**) in 85 and 65% yield (Scheme 2). Both are thermally robust air-stable compounds in solution and in the solid state. Characterization was by elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In addition, **3** has also been characterized by IR spectroscopy. The ^{1}H NMR spectrum of **3** displays an AB pattern for the CH_2Ph moiety showing two doublets centered at 5.12 and 4.76 ppm with a coupling constant of 13.9 Hz. Characteristic ^{13}C{^{1}H} NMR spectroscopic features of **3** and **4** comprise marked low-field resonances at 288.0 and 293.5 ppm, respectively, assignable to the carbene carbon atom of the =CCH_2R-aapy moiety. In the IR spectrum the C=O stretching frequency observed at 1748 cm^{-1} indicates the absence of the dipolar imine structure (e.g. in **2a** $\nu_{C=O}$ is 1656 cm^{-1}). The structure of **3** in the form of its solvate **3**·$^1/_2(C_2H_5)_2O$ contains two crystallographically independent Ru complexes and one well-ordered solvent molecule in the asymmetric unit of the triclinic cell. The two complexes are stereochemically closely similar at the metal center but differ distinctly in the orientations of their benzyl termini. The environment about ruthenium corresponds to a slightly distorted octahedron, as shown in Figure 2, which is very similar to those of **2b** and most other RuTp complexes. However, the two Ru−N(Tp) bond distances cis to the carbene moiety are significantly shorter (Ru(1)−N(2) = 2.061(2) Å, Ru(1)−N(4) = 2.081(2) Å; Ru(2)−N(10) = 2.066(2) Å, Ru(2)−N(12) = 2.090(2) Å) than the one *trans* to the carbene unit (Ru(1)−N(6) = 2.216(2) Å; Ru(2)−N(14) = 2.220(2) Å) due to the strong *trans* influence of the strong π-accepting carbene. The Ru(1)−N(7) and Ru(1)−Cl(1) bond lengths are 2.045(2) and 2.416(1) Å, respectively (Ru(2)−N(15) = 2.042(2) Å, Ru(2)−Cl(2) = 2.385(1) Å). The Ru(1)−C(17) bond distance of 1.897(2) Å (Ru(2)−C(41) = 1.878(2) Å) is comparable to those of other heteroatom-stabilized ruthenium carbene complexes.[2,3]

Treatment of **2a** with HC≡CR (R = C(Me)(Ph)OH, C_6H_{11}) results in the formation of the vinylcarbene complexes RuTp(=CCH=C(Me)Ph-aapy)Cl (**5**) and RuTp(=CCH=C_6H_{10}-aapy)Cl (**6**), while in the case of R = COOEt and COOMe, the olefin complexes RuTp(aapy-CH=CHCOOEt)Cl (**7**) and RuTp(aapy-CH=CHCOOMe)Cl (**8**) are obtained. For the last two substituents, the

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(15) Burns, I. D.; Hill, A. F.; Williams, D. J. *Inorg. Chem.* **1996**, *35*, 2865.

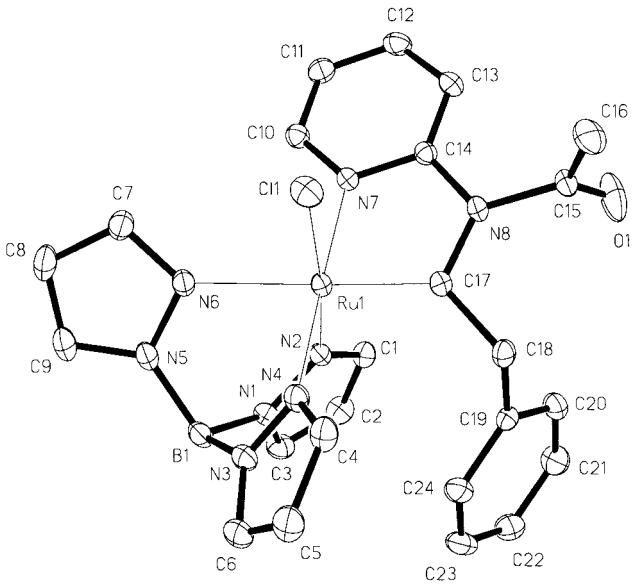

Figure 2. Structural view of RuTp(=CCH_2Ph-aapy)Cl·$^1/_2O(C_2H_5)_2$ (**3**·$^1/_2O(C_2H_5)_2$). Only one of the two crystallographically independent complexes is shown. Selected bond lengths (Å) and angles (deg): Ru(1)−C(17), 1.897(2); Ru(1)−N(2), 2.061(2); Ru−N(4), 2.081(2); Ru(1)−N(6), 2.216(2); Ru(1)−N(7), 2.045(2); Ru(1)−Cl(1), 2.416(1); C(17)−N(8), 1.387(3); N(8)−C(15), 1.465(3); N(8)−C(14), 1.398(3); C(17)−N(8)−C(15), 125.1(2); N(8)−C(15)−O(1), 120.0(2); Ru(1)−C(17)−N(8), 115.2(1); Ru(1)−C(17)−C(18), 130.3(2); N(2)−Ru(1)−N(4), 88.3(1); N(4)−Ru(1)−N(6), 83.1(1); N(2)−Ru(1)−N(6), 85.3(1); C(1)−Ru(1)−Cl(1), 90.7(1).

initially formed carbene complexes RuTp(=CCH_2R)(Cl) (eqs 1−3) apparently rearrange to give the thermodynamically more stable complexes **5**−**8**. The compounds **5** and **6** form vinylcarbenes through elimination of H_2O and a 1,3-hydrogen shift (eqs 1 and 2), whereas **7** and **8** are formed via a 1,2-hydrogen shift (eq 3). The latter process is a common decomposition pathway of electron-deficient carbene complexes. In fact, only the carbene intermediates of the most strongly electron-withdrawing R groups, viz. COOEt and COOMe, are found to undergo this isomerization. In the complexes **7** and **8** four coordination sites are occupied by Tp and chlorine, and the two remaining positions are taken by the chelating aapy-CH=CHCOOEt ligand coordinated via the pyridine nitrogen atom and the C=C bond. The −CH=CH− moiety adopts a *cis* conformation, as is apparent from the ^{1}H NMR spectrum, showing two doublets centered at 7.79 ($^3J_{HH}$ = 8.8 Hz) and 3.65 ($^3J_{HH}$ = 8.8 Hz) ppm for **7** and 7.81 ($^3J_{HH}$ = 9.3 Hz) and 3.63 ($^3J_{HH}$ = 9.3 Hz) ppm for **8**.

The formation of the amidocarbene complexes above likely proceeds via vinylidene intermediates according to Scheme 2, with or without participation of the isomeric imine form of Haapy. Although such intermediates could not be isolated or detected spectroscopically, the tendency of vinylidene complexes to be readily attacked by nitrogen or oxygen donors to give Fischer type carbene complexes is well-known.[2d,3a,4] Such a process would be especially facile when the nucleophilic attack occurs in an intramolecular, chelate-assisted fashion so as to overcome steric limitations.[16] This explains the otherwise highly unexpected attack of the very weakly nucleophilic nitrogen of an acid amide.

Since amido carbene complex formation necessarily involves proton migration, it might be surmised that this reaction is prevented when the *N*-ethyl derivative of Haapy is used, requiring the much more unfavorable ethyl migration. In fact, the reaction of RuTp(N-Et-4-Me-Haapy)Cl (**2c**), prepared analogously, with HC≡CPh did not yield the amido carbene complex (nor the originally wanted neutral vinylidene complex) but only polymeric products.[8b] It would appear that the present chelate ligand is not labile enough to be opened under moderate reaction conditions. Thus, the high temperature needed for conversion gives rise to two reaction pathways, the one being full substitution of the py ligand with subsequent polymerization of the acetylene, and the other being the formation of the chelate-stabilized and hence unreactive amidocarbene complex.

In summary, we have shown that acetamidopyridines are hemilabile ligands promoting the formation of vinylidene complexes. The strong electrophilic character of the α-carbon atom of the vinylidene unit is demonstrated in that even the weakly nucleophilic nitrogen atom of the acid amide reacts readily with the vinylidene moiety in an intramolecular fashion to give cyclic amido carbene complexes.

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, all bond lengths and angles, and least-squares planes for **2b**·CH_2Cl_2 and **3**·$^1/_2O(C_2H_5)_2$ (12 pages). Ordering information is given on any current masthead page.

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